

New Journal of Chemistry

Activation of Carbon Dioxide by New Mixed Sandwich Uranium(III) Complexes
Incorporating Cyclooctatetraenyl and Pyrrolide, Phospholide, or Arsolide Ligands

Rachel J. Kahan,^a F. Geoffrey N. Cloke,^{a*} S. Mark Roe^a and François Nief^b

^aDepartment of Chemistry, School of Life Sciences, University of Sussex, Brighton, BN1
9QJ, UK; ^b École Polytechnique, CNRS, Route de Saclay, F-91128 Palaiseau, France.

Electronic Supplementary Information

Cyclic voltammetry

Studies were conducted in an MBraun glovebox under argon using a BASi Epsilon-EC potentiostat under computer control. iR drop was compensated for by using the feedback method. All experiments were conducted using a gold disc (2.0 mm²) or glassy carbon disc (7.0 mm²) working electrode, platinum wire counter electrode and silver wire pseudo-reference electrode. Ferrocene (*ca.* 1 mg) was added to all solutions after initial voltammograms had been obtained to obtain the [FeCp₂]⁺⁰ reference couple. Samples were prepared by dissolving the analyte (5 – 10 mM) in a solution of supporting electrolyte (5 mM [ⁿBu₄N][B(C₆F₅)₄] in 1 ml THF). Studies of **1** showed five electrochemical events, of which four were stable over 5 cycles. The fifth event at -0.05 V *vs* FeCp₂⁺⁰ diminished with successive scans. Studies of **2** showed two quasi-reversible waves (process 3 and 4) and one distorted wave, all of which were stable over a minimum of four cycles. Complex **3** exhibited three distorted waves, which were also stable over several cycles. Distortion of the waves prevented determination of $E_{1/2}$ for some processes. All reported potentials are referenced to the FeCp₂⁺⁰ redox couple, which was measured by addition of ferrocene (*ca.* 1 mg) to the solution after all initial voltammograms had been obtained.

Compound	Process 1 $E_{1/2}$ /V	Process 2 $E_{1/2}$ /V	Process 3 $E_{1/2}$ /V	Process 4 $E_{1/2}$ /V	Process 5 $E_{1/2}$ /V
1	-2.50	-1.88	-1.42	-0.62	-0.05
2		-1.92 ^a	-1.32	-0.81	
3		-1.89 ^a	-1.26 ^b	-0.71 ^b	

Table S1 Electrode potentials *vs* FeCp₂⁺⁰ in 0.05 M [ⁿBu₄N][B(C₆F₅)₄]/THF at 100 mV·s⁻¹.

^aEp_c values given instead of $E_{1/2}$; ^bEp_a values given instead of $E_{1/2}$.

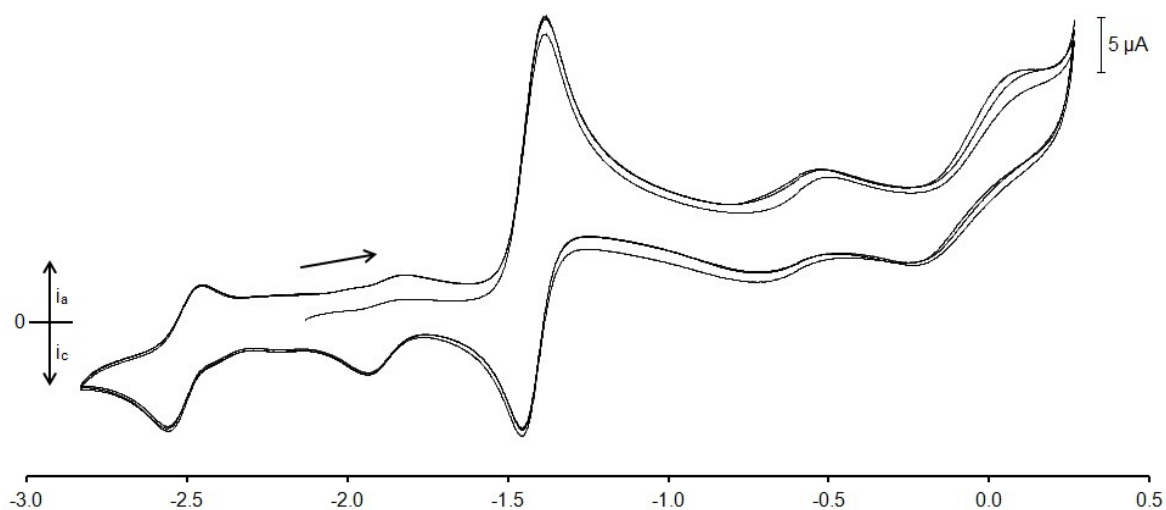


Figure S1: Overlaid CV scans (3 cycles) of $[U(COT^{TIPS2})(Cp^{NMe4})]$ (1) in 0.05 M $[nBu_4N][B(C_6F_5)_4]$ /THF at $100 \text{ mV} \cdot \text{s}^{-1}$.

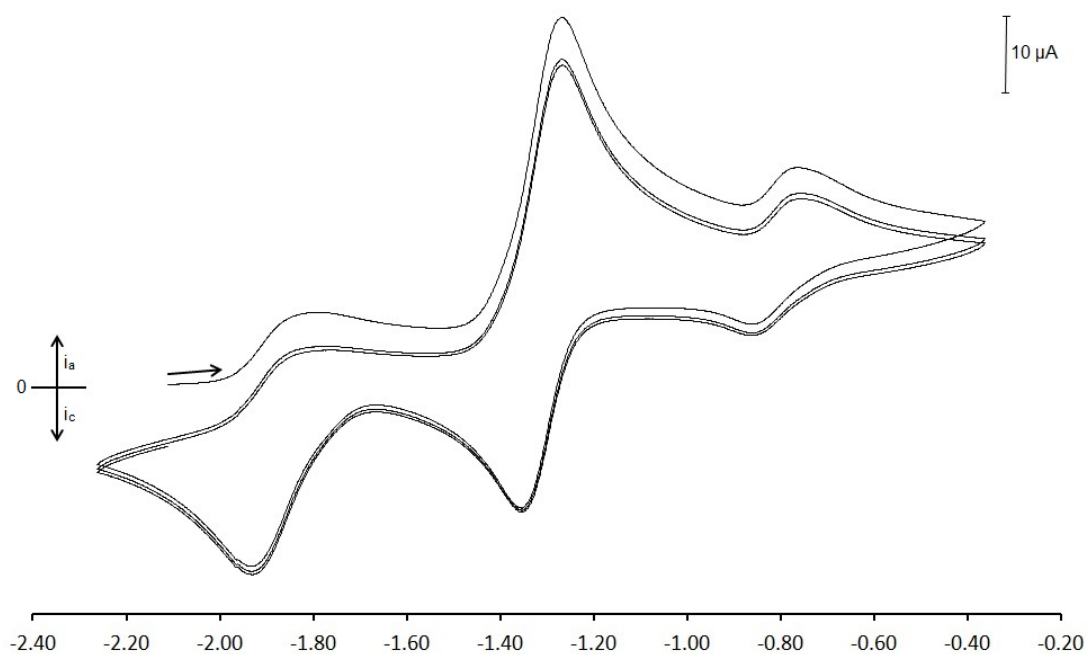


Figure S2: Overlaid CV scans (3 cycles) of $[U(COT^{TIPS2})(Cp^{PMe4})]$ (2) in 0.05 M $[nBu_4N][B(C_6F_5)_4]$ /THF at $100 \text{ mV} \cdot \text{s}^{-1}$.

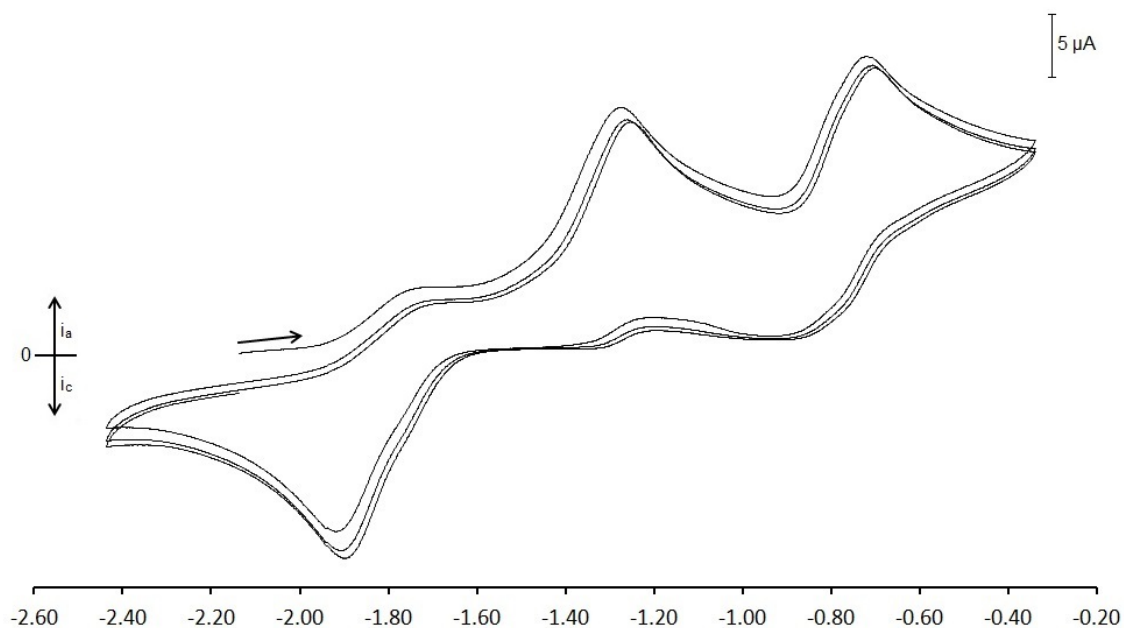


Figure S3: Overlaid CV scans (3 cycles) of $[\text{U}(\text{COT}^{\text{TIPS}2})(\text{Cp}^{\text{AsMe}4})]$ (**3**) in 0.05 M $[\text{nBu}_4\text{N}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{THF}$ at $100 \text{ mV} \cdot \text{s}^{-1}$.

X-ray Crystallographic Studies

Data for **1**, **2**, **3** and **5** were collected on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$) source, and data for **1**·THF were collected using a Agilent Technologies Xcalibur Gemini ultra diffractometer with a Cu K α radiation ($\lambda = 1.54184$) source at 173 K using an Oxford Cryosystems Cobra low temperature device, operating in ω scanning mode with ψ and ω scans to fill the Ewald sphere. The programs used for control and integration were Collect,¹ Scalepack and Denzo.² Absorption corrections were based on equivalent reflections using SADABS.³ Data for **4** were collected and processed by the UK National Crystallography Service at the University of Southampton. The crystals were mounted on a glass fibre with silicon grease, from dried vacuum oil kept over 4 Å molecular sieves in an MBraun glovebox under Ar. All solutions and refinements were performed using the WinGX⁴ or Olex2⁵ packages and software therein. All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were refined using a riding model. Complex **1** could not be collected at high resolution, and the structure only illustrates connectivity. **2** and **3** exhibit disorder of the five-membered ring over two positions. This has been modelled in **2** to illustrate the two positions and has been modelled in **3** by keeping one of the ring carbon atoms isotropic. **4** crystallises with several molecules of hexane in the unit cell which has been modelled using the

SQUEEZE⁶ function in PLATON.⁷ Several atoms have been made isotropic due to positional disorder within the *iso*-propyl groups. Structural and refinement details are presented in the following tables.

Compound	1	1·THF	2·THF	3·THF
Colour, Habit	Purple, Needle	Brown, Needle	Purple, Needle	Brown Rod
Size /mm	0.10 x 0.12 x 0.18	0.02 x 0.04 x 0.10	0.06 x 0.12 x 0.62	0.04 x 0.06 x 0.18
Empirical Formula	C ₆₈ H ₁₂₀ N ₂ Si ₄ U ₂	C ₃₈ H ₆₈ NOSi ₂ U	C ₃₈ H ₆₈ OPSi ₂ U	C ₃₈ H ₆₈ OASi ₂ U
M	1554.09	849.14	866.10	910.05
Crystal System	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space Group	Pbc21	P21/n	P21/n	P21/n
a /Å	12.5424(1)	11.8517(2)	11.8847(7)	11.9699(2)
b /Å	22.7691(3)	14.9317(2)	14.9475(8)	14.9384(2)
c /Å	24.9695(2)	22.2479(3)	22.5236(14)	22.3339(4)
α /°	90	90	90	90
β /°	90	91.366(2)	89.568(5)	90.5380(10)
γ /°	90	90	90	90
V /Å ³	7130.77(12)	3936.00(10)	4001.1(4)	3993.36(11)
Z	8	4	4	4
μ /mm ⁻¹	4.641	12.386	4.183	4.973
T (K)	173.15	173.15	173.15	173.15
θmin/max	1.62, 27.48	3.565, 61.153	3.429, 29.374	1.64, 27.47
Completeness	0.999, 27.48	0.995	0.872, 29.374	0.999
Reflections Total/Independent	96143 / 15976	21216 / 6020	34897 / 9625	53555 / 9140
Rint	0.0649	0.0504	0.0460	0.0843
Final R1 and wR2	0.0333, 0.0765	0.0539, 0.1539	0.0291, 0.0613	0.0396, 0.1146
Largest peak hole/ e. Å ⁻³	0.873 / -1.900	6.613 / -2.035	1.03/-0.97	1.297 / -2.231
ρcalc/g.cm ⁻³	1.448	1.433	1.438	1.514

Compound	4	5
Colour, Habit	Orange, Plate	Red Prism
Size /mm	0.01 x 0.06 x 0.07	0.06 x 0.08 x 0.12
Empirical Formula	C ₇₀ H ₁₂₀ N ₂ O ₅ Si ₄ U ₂	C ₇₀ H ₁₂₀ O ₅ Si ₄ P ₂ U ₂
M	1658.11	1692.03
Crystal System	Triclinic	Monoclinic
Space Group	P-1	P21/c
a /Å	12.9610(9)	22.3131(4)
b /Å	14.6337(10)	15.0442(3)
c /Å	22.2106(16)	22.7699(4)
α /°	97.035(6)	90
β /°	97.053(6)	96.826(1)
γ /°	102.983(7)	90
V /Å ³	4024.5(5)	7589.3(2)
Z	2	4
μ /mm ⁻¹	4.121	4.412
T (K)	173.15	173.15
θ min/max	2.430, 27.562	3.439, 27.492
Completeness	97.7, 27.562	0.988
Reflections Total/Independent	47825 / 18150	53555 / 9140
Rint	0.0794	0.0843
Final R1 and wR2	0.0703, 0.1751	0.0550, 0.1586
Largest peak hole/ e. Å ⁻³	4.02/-2.64	1.159 / -8.442
ρ calc/g.cm ⁻³	1.368	1.514

CCDC 1051779-1051784 contain the supplementary crystallographic data for this paper.

¹ Collect, Bruker-AXS, Madison, WI, 1997–2004.

² Z. Otwinowski, W. Minor and W. SCALEPACK and DENZO, *Methods Enzymol.*, 1997, **276**, 307.

-
- ³ G. M. Sheldrick, *SADABS V2008/1*, University of Göttingen, Göttingen, Germany.
- ⁴ O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- ⁵ L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
- ⁶ P. Van Der Sluis and A. L. Spek, *Acta Crystallogr., A, Found. Crystallogr.*, 1990, **46**, 194–201.
- ⁷ A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.